Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary Information

A New Organic-Inorganic Hybrid Based on the Crescent-Shaped Polyoxoanion $[H_6SiNb_{18}O_{54}]^{8-}$ and Copper-Organic Cations

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1. Materials and Methods

All the chemicals were obtained from commercial sources, and were used without further purification. Elemental analyses (C, H, N) were measured on a Perkin-Elmer 2400 CHN elemental analyzer; Nb, Si and Cu were determined with a Plasma-SPEC(I) ICP atomic emission spectrometer. IR spectrum was performed in the range 4000–400 cm^{-1} using KBr pellets on an Alpha Centaurt FT/IR spectrophotometer. Powder X-ray diffraction measurement was recorded radiation ranging from 5 to 50º at room temperature on a Siemens D5005 diffractometer with Cu-Kα (λ = 1.5418 Å). Thermogravimetric analysis (TGA) of the samples was performed using a Perkin-Elmer TG-7 analyzer heated from room temperature to 900 ºC under nitrogen at the heating rate of 5 °C·min^{-1}.

2. Synthesis

Syntheses of **1**: $K_7HNb_6O_{19}\cdot 13H_2O$ was prepared according to the literature method and identified by IR spectra.[1] Ethylenediamine (0.003 g, 0.050 mmol) was added to the solution of $Cu(Ac)_2\cdot 3H_2O$ (0.024 g, 0.100 mmol) in water (5 mL) under stirring. Then the resulting blue solution was added dropwise to the solution of $K_7HNb_6O_{19}\cdot 13H_2O$ (0.137 g, 0.100 mmol) and $Na_2SiO_3\cdot 9H_2O$ (0.057 g, 0.200 mmol) in water (10 mL) under stirring. Subsequently, the mixture was adjusted to pH 11 using NaOH (1 $molL^{-1}$) solution and was transferred into a 23 mL Teflon-lined stainless steel container and heated at 160 ℃ for 72 hours. After cooling to room temperature, the block-shaped purple crystals of **1** were collected by filtration. Yield: 39 mg (32.1% based on Nb). Elemental analysis: Anal. Calc.: C 5.24%; H 2.25%; N 6.11%. Found: C 5.40%; H 2.44%; N 6.33%.

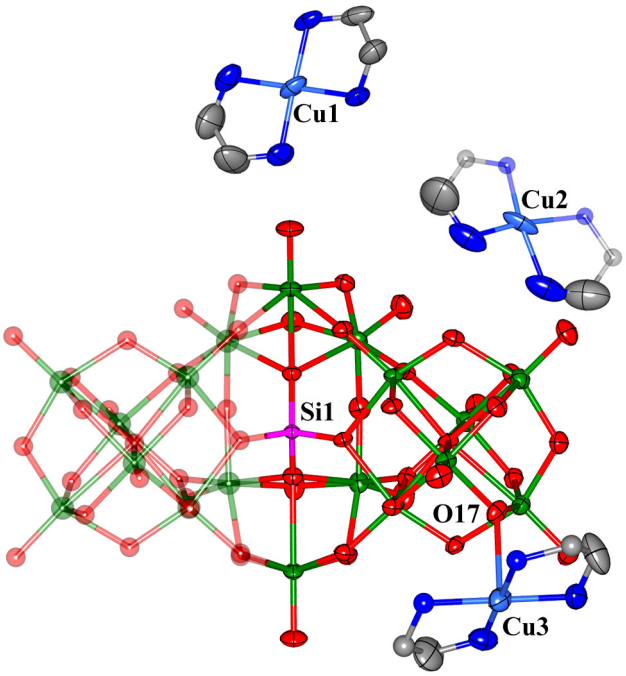

Fig. S1. ORTEP diagram showing the asymmetric unit of compound **1** with thermal ellipsoids at 50% probability.

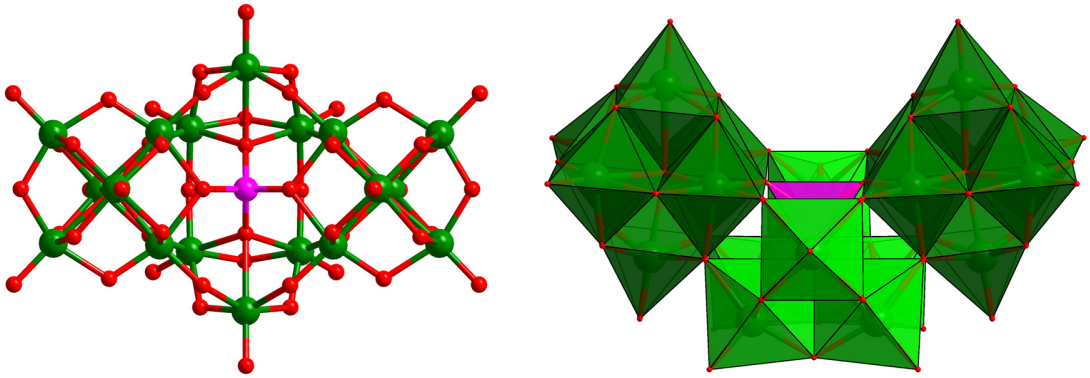

Fig. S2. Ball-and-stick and polyhedral representations of the polyoxoanion $[H_6SiNb_{18}O_{54}]^{8-}$.

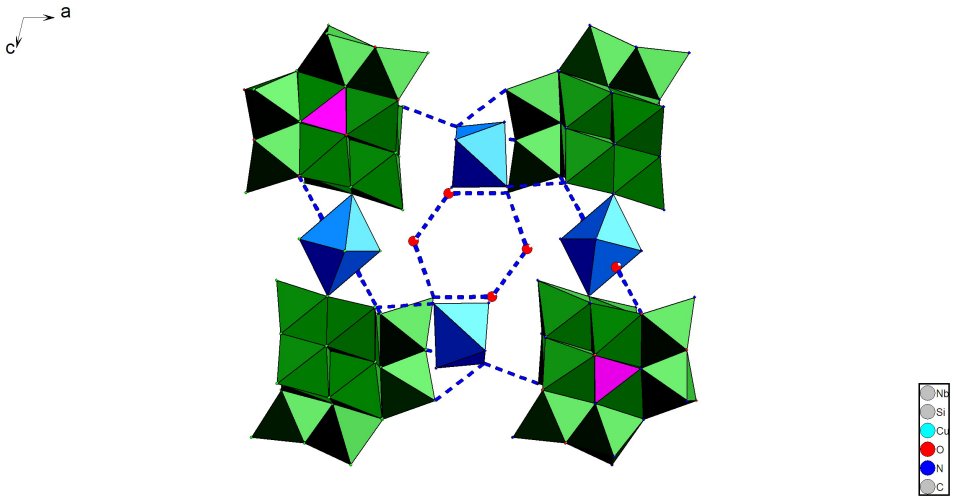

Fig. S3. The H-bond of the 3D supramolecular structure.

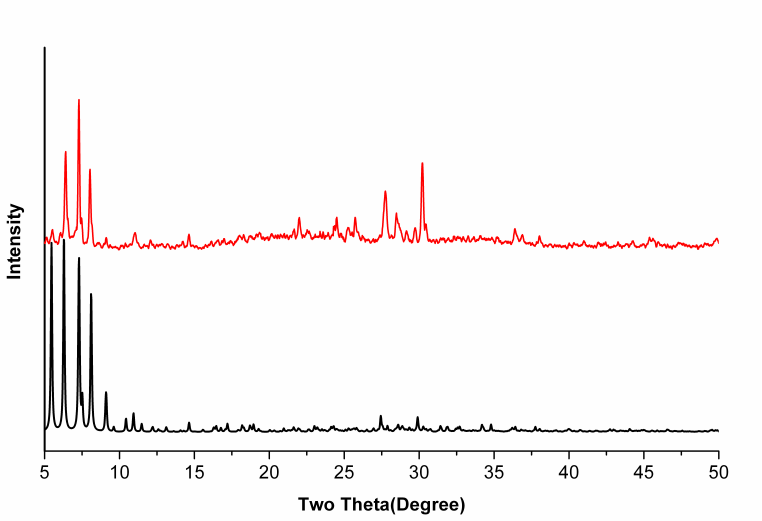

Fig. S4. The XRPD pattern (top) and simulated pattern (bottom) of **1**.

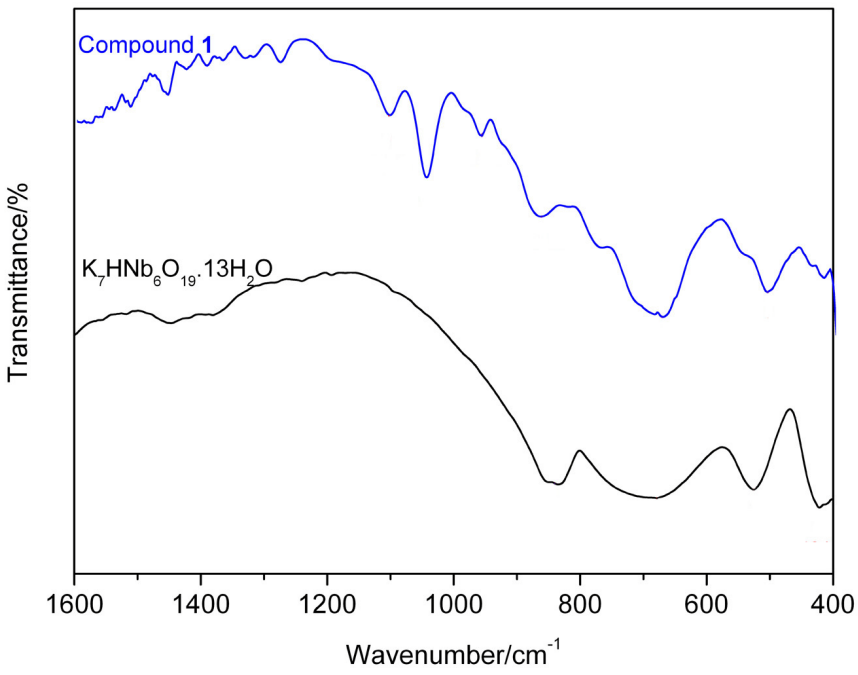

Fig. S5. The IR spectrum of **1**.

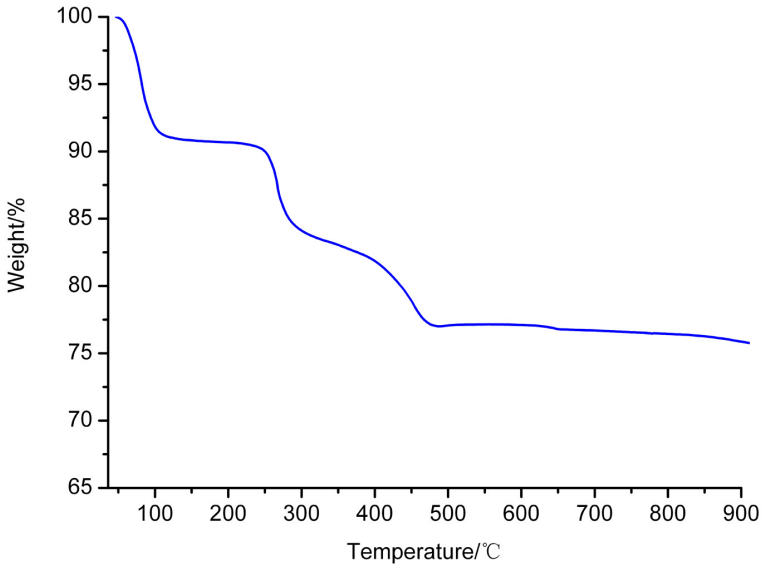

Fig. S6. The TG curve of **1**.

References

1 M. Filowitz, R. K. C. Ho, W. G. Klemperer, W. Shum, *Inorg. Chem.,* 1979, **18**, 93.